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Rapid measurement of boiling points and vapor pressure of binary mixtures of short-chain triglycerides by TGA method

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Abstract

Thermogravimetric analysis (TGA), has been used to rapidly obtain data on the temperature dependence of vapor pressure (760, down to 20 mmHg) and the boiling points for simple binary mixtures of tributyrin (C4 : 0), tricaproin (C6 : 0) and/or tricaprylin (C8 : 0). Vapor-pressure measurements were taken for binary mixtures of the aforementioned compounds as a function of mole fraction. Additional measurements of methyl esters of rapeseed oil and tallow, ''biodiesel'', were included for comparison. The resulting data were then compared to the projected behavior of ideal mixtures of the same components. These measurements were then used to determine the effective heat of vaporization, ΔH_v. © 1998 Elsevier Science B.V.

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1. Introduction

The temperature dependence of vapor pressure and the nominal boiling point at one atmosphere are of interest in predicting the pressure atomization characteristics of substitute diesel fuels based on triglycerides or methyl esters. From vapor-pressure data, one may calculate the heat of vaporization, ΔH_v, which, in turn, may also be used to estimate atomization characteristics of fuels [1]. Previous reports have examined the other characteristics of the pure short-chain triglycerides studied in this paper [2]. These experiments have produced consistent results which could provide a basis for models which predict atomization properties of different triglyceride combinations. These models may then ultimately be used to predict the performance of possible alternative diesel fuels.

Since some promising substitute diesel fuels consist of mixtures of triglycerides, the vapor pressure and effective heat of vaporization of simple triglyceride mixtures are valuable tools in determining the suitability of such mixtures as fuels. The thermal properties of binary mixtures of liquids generally place them into one of the two solution types. The first of these are ideal solutions. These types of solutions exhibit uniform, predictable thermal properties and generally occur when the two-component liquids have similar chemical properties. In contrast, non-ideal solutions display non-uniform thermal properties which can vary in complexity. The binary mixtures examined

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in this study should exhibit near-ideal solution behavior since the chemical properties of the components are quite similar.

Although the study of binary mixtures of triglycerides can provide a basis for models predicting the behavior of more complex mixtures, ultimately the predictions inferred from the ideal-solution models will need to be tested. For this reason, thermal properties of esters from tallow and rapeseed oil, successfully used as biodiesel substitute-diesel fuels, have also been examined. The components of such esterified oils exhibit a wider range of chemical properties than simple binary mixtures. One might reasonably expect the esters to fractionate, with several boiling-point steps on the TGA output. Alternatively, the boiling points may not be resolved, and a single average boiling point may be observed. The data gathered on esters may serve to test the models created from the examination of simple mixtures as well as provide data on physical property for the methyl ester products.

Thermogravimetric analysis (TGA) was shown to be a rapid means of quantifying vapor pressure of selected organic compounds, including triglycerides [3]. Samples were sealed in aluminum capsules with a laser-drilled opening in the lid. Vapor pressure data were taken at temperatures between 25° and 400°C and at pressures from ambient down to 20 mmHg. The laser-drilled opening permitted vapor pressure balance between the sample and the controlled environment pressure. An inert diluent, powdered alumina, reduced the rate of vaporization as the sample approached its boiling point and reduced superheating tendencies [4].

The primary objective of this study was to use ≈5 mg samples to rapidly obtain vapor pressures and boiling points for binary mixtures of the short-chain triglycerides: tributyrin (C4 : 0), tricaproin (C6 : 0) and tricaprylin (C8 : 0). The results of these experiments were then compared to the behavior of ideal solutions of the components. Another objective concerned TGA data on complex methyl ester mixtures, "biodiesel", presently being evaluated as diesel fuels. The vapor pressures of two biodiesel fuels, tallow ethyl ester and rapeseed methyl ester, were determined using the TGA method and the data was then compared to that of the simple mixtures examined here.

2. Equipment and procedure

Thermogravimetric analysis (TGA) data were obtained with a TA Instruments Model 951 thermobalance with a quartz furnace tube. At ambient pressure, a 50 ml/min nitrogen purge flow was used. Subatmospheric pressures were obtained with a mechanical vacuum pump (Edwards, model 5, 2 stage) and manually controlled air-flow restriction valves. The platinum sample support was reshaped to accommodate the laser-drilled aluminum capsules obtained from Perkin–Elmer (Part No. N5190788). The drilled openings are 0.050–0.100 mm in diameter [5,6]. The sample holders were sealed shut using the volatile sealer assembly recommended by the manufacturer (Part No. 0219-0061). Consistent sealing was achieved by using a torque wrench with a socket fabricated to fit over the sealing unit mechanism. A force of 3.05 Nm (∓0.23 Nm) was applied to achieve the most effective seal. Torque required may depend on shear strength of aluminum capsule material.

A thermocouple was placed immediately outside the platinum holder for all runs, following TA Instruments recommendations. Samples (≈6.0±1 mg) were placed in 20 μl pans with laser-drilled covers. To assist in achieving isothermal boiling, ≈3 mg of alumina powder was added to the sample as an inert diluent. The heating rate was set at 10°C/min. Each experiment was conducted at constant pressures measured with a calibrated strain-gage-type manometer from SenSym (model PDM 200M). Pressure was maintained at ±1.0 mmHg by manually adjusting a micrometer-type air bleed valve.

The sample weight loss was determined as the difference between the initial and final weight. The boiling point at each pressure is taken as the onset of isothermal boiling. This point is the intersection of the tangent of the isothermal weight-loss slope with the initial base line as shown in Fig. 1. The TA Instruments data-analysis software quickly determines this onset temperature. The initial baseline was steady for all runs which suggests that there was no chemical decomposition before the boiling point was reached.

To check the accuracy of the TGA unit for vapor pressure of mixtures, a mixture of well-characterized compounds, Nonanol and Decanol, was selected as a standard reference for near-ideal binary solutions [7].

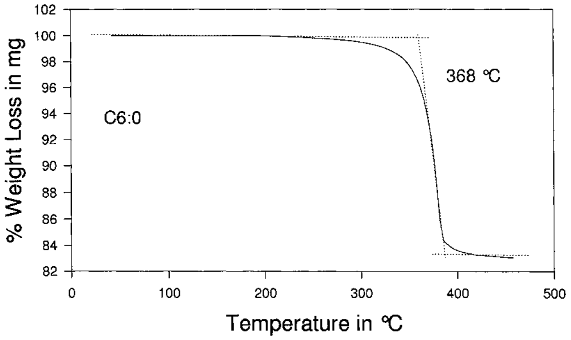

Fig. 1. Example of TGA data plot, showing tangents used to locate onset temperatures.

In view of reports by [5,6] on the laser-drilled capsules, reference materials were chosen to have molecular weights, boiling points, viscosities, and chemical functional groups similar to the compounds under study.

Reference curves were generated for ideal mixtures by determining the partial pressure of each component triglyceride vs. temperature using the Clausius–Clapeyron equation determined by linear regression of experimental data, as described below. The resulting pressure data was then substituted in Eq. (1) to give the mole fraction of the component with the higher boiling point:

$$P_{\mathrm{tot}} = P_{\mathrm{A}}X_{\mathrm{A}} + P_{\mathrm{B}}(1 - X_{\mathrm{A}}) \qquad (1)$$

where P_{A} and X_{A} are the partial pressure and mole fraction of the component with the lower boiling point, respectively, and P_{B} the partial pressure of the other component. The resulting mole fraction data was then plotted against temperature to produce the curves for the ideal solutions.

Vapor-pressure data was collected for three binary mixture schemes: tributyrin (C4 : 0) and tricaproin (C6 : 0), tributyrin (C4 : 0) and tricaprylin (C8 : 0), and tricaproin (C6 : 0) and tricaprylin (C8 : 0). Tributyrin (98%, MW 302.37 g/mol, CAS# 60-01-5) was supplied by Aldrich. Tricaproin (99%, MW 386.5 g/mol, CAS# 621-70-5) and Tricaprylin (97.5%, MW 470.7 g/mol, CAS# 538-23-8) were supplied by Sigma. Vapor-pressure data was also collected for tallow ethyl ester (TEE) and rapeseed methyl ester (RME) supplied by Charles Peterson of the University of Idaho. Nonanol was supplied by Sigma, (98%, MW 144.3 g/mol) and decanol was supplied by Aldrich (99%, MW 158.3 g/mol). Alumina powder was from Baker, chromatography grade.

3. Results and discussion

3.1. Nonanol/decanol as a reference mixture

Nonanol/decanol mixtures were used to examine the vapor-pressure behavior of an ideal solution in the TGA. Five compositions were examined at atmospheric pressure and one of these, x=0.73, was examined at reduced pressures (see Figs. 2 and 3). The shape of the TGA curves for all these mixtures was remarkably similar to those of a pure compound. In Fig. 2, an ideal solution curve was generated using boiling-point data from Perry [7] for nonanol and decanol (see Section 2). The vapor pressure of nonanol/decanol mixtures is composition dependent and closely follows the ideal-solution vapor-pressure curve. The average deviation from the ideal vapor-pressure curve was only 0.3%. For Fig. 3 (x=0.73), The correlation coefficient (R_2=0.99) for the linear Clausius–Clapeyron plot strongly suggests that this reference ideal solution is vaporizing at pseudo-constant temperatures [8]. Both sets of measurements indicate that the TGA method performs accurately with vapor pressure determinations for near-ideal solutions.

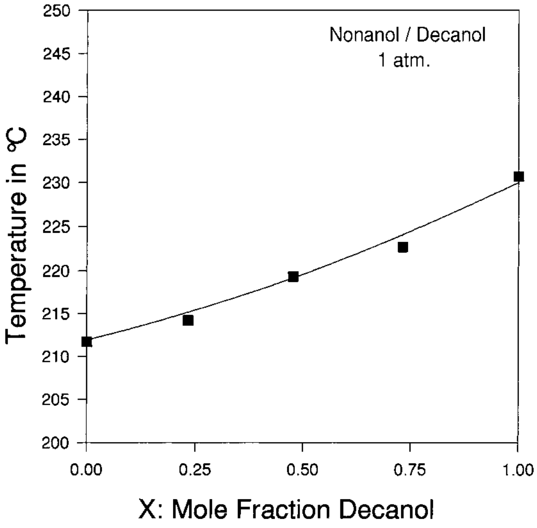

Fig. 2. TGA-derived 1 atm boiling points for mixtures of nonanol/decanol.

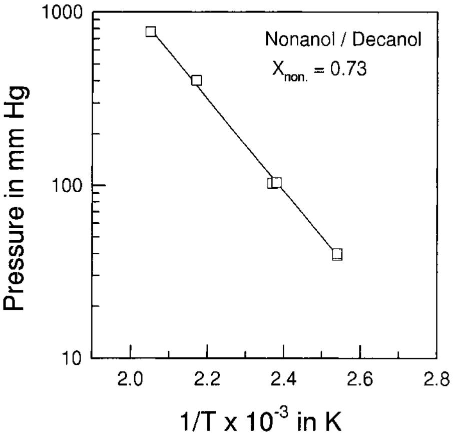

Fig. 3. TGA-derived 1 atm temperature dependance of vapor pressure for mixtures of decanol and nonanol.

3.2. Boiling point vs. composition

The boiling point at one atmosphere for each of the three triglyceride mixtures was determined for at least five mole fractions. The percent deviation for replicate runs averaged 2.0%. The average deviation from the ideal-solution curve was 1.1%. Typically, runs had single transitions whose temperature intervals were proportional to the narrow interval shown in Fig. 1. The results for each mixture are given in Tables 1–3. Also included are the ideal boiling points taken from the ideal-solution boiling-point curve generated using the vapor pressures of pure components [9]. The percent deviation of the experimental average values from the ideal values is included on these tables.

Table 1
TGA-derived 1 atm boiling points for mixtures of C4 : 0 and C6 : 0

C6 mole fraction	Boiling point/ °C	Observed boiling point/ °C	Ideal boiling point/ °C	Deviation [a]/ %
0.00	317.4			
0.00	315.00	316.2	317.93	0.5 [b]
0.10	317.94			
0.10	313.40	315.67	320.95	1.6
0.21	325.60			
0.21	323.65			
0.21	326.37	325.21	324.82	0.1
0.44	330.04			
0.44	335.16	332.6	334.77	0.6
0.70	346.35			
0.70	340.66	343.51	349.06	1.6
0.85	358.59			
0.85	360.70	359.4	358.77	0.2
1.00	368.20			
1.00	368.10	368.15	369.55	0.4 [b]

[a] Boiling-point deviation, $(T_{obs}-T_{ideal})/T_{ideal}$, where T_{obs} is data at composition X_i and T_{ideal} the boiling point of an ideal mixture at X_i.
[b] End point deviations are due to slight misfit between ideal vapor-pressure regression and boiling point of pure liquids.

Table 2
TGA-derived 1 atm boiling points for mixtures of C4 : 0 and C8 : 0

C8 mole fraction	Boiling point/ °C	Observed boiling point/ °C	Ideal boiling point/ °C	Deviation [a]/ %
0.00	317.4			
0.00	315.00	316.2	317.97	0.6 [b]
0.18	319.56			
0.18	316.66	317.61	325.73	2.5
0.39	333.99			
0.39	337.92	335.96	337.15	0.4
0.52	360.42			
0.52	358.33	359.38	345.50	4.0
0.66	363.94			
0.66	371.20			
0.66	369.79	368.31	355.58	3.6
0.82	378.28			
0.82	379.95	379.1	368.50	2.9
1.00	385.2			
1.00	385.3	385.25	384.80	0.1 [b]

[a] Refer Table 1, footnote (a).
[b] Refer Table 1, footnote (b).

Representative TGA data are plotted in Figs. 4–6. These figures allow a graphic comparison of the experimental data with the behavior of an ideal solution. It should be noted that the misfit between the data and the ideal-solution curve changes with each mixture. The experimental data for the tricaproin/tricaprylin mixture most closely fits the ideal-solution curve. In contrast, the tributyrin/tricaprylin mixture data show pronounced deviation from the ideal curve. In fact, this mixture exhibits a sinusoidal behavior which is not seen in the other two mixtures. The plot for the mixture of tributyrin and tricaproin reveals behavior somewhere in-between the other two mixtures. Since tricaproin and tricaprylin have similar chemical properties while tributyrin and tricaprylin are quite different chemically, it appears that as the chemical similarity of the compounds increases, the behavior of the mixture tends to resemble more an ideal solution, as predicted by Moore [9].

Table 3
TGA-derived 1 atm boiling points for mixtures of C6 : 0 and C8 : 0

C8 mole fraction	Boiling point/ °C	Observed boiling point/ °C	Ideal boiling point/ °C	Deviation [a]/ %
0.00	368.2			
0.00	368.1	368.15	370.24	0.6 [b]
0.05	369.57			
0.05	370.63	370.10	371.20	0.3
0.10	369.11			
0.10	369.48	369.30	371.90	0.7
0.21	369.47			
0.21	369.63	369.55	373.65	1.1
0.45	368.93			
0.45	376.01	372.47	377.32	1.3
0.71	375.82			
0.71	383.24	379.53	381.00	0.4
1.00	385.2			
1.00	385.3	385.25	384.77	0.1 [b]

[a] Refer Table 1, footnote (a).
[b] Refer Table 1, footnote (b).

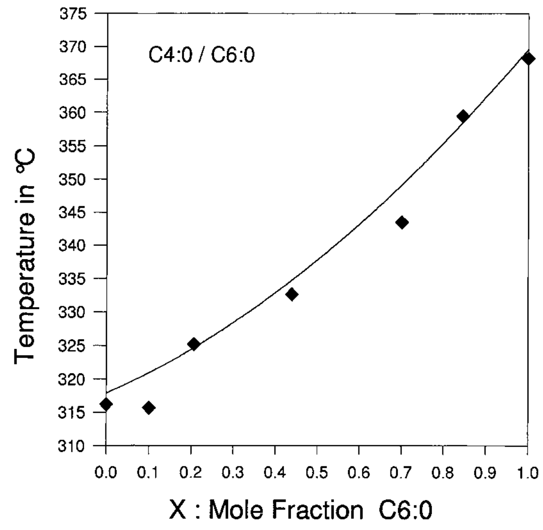

Fig. 4. TGA-derived 1 atm boiling points for mixtures of C4 : 0 and C6 : 0.

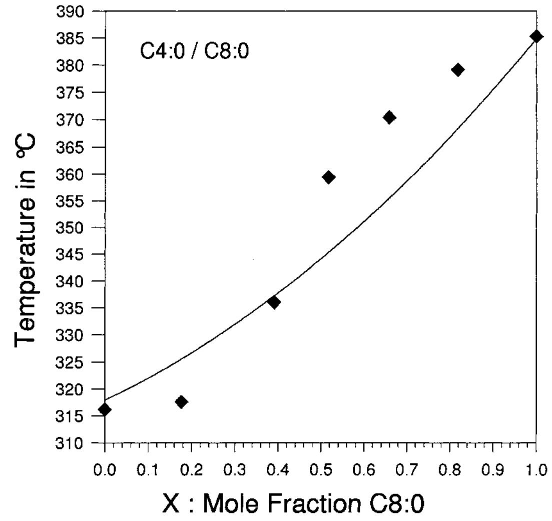

Fig. 5. TGA-derived 1 atm boiling points for mixtures of C4 : 0 and C8 : 0.

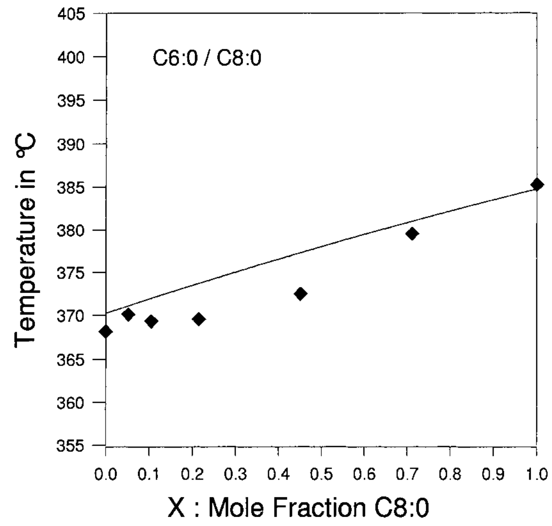

Fig. 6. TGA-derived 1 atm boiling points for mixtures of C6 : 0 and C8 : 0.

The boiling-point deviation of these mixtures was calculated as follows:

$$\text{Deviation} = (T_{\text{obs}} - T_{\text{ideal}})/T_{\text{ideal}} \qquad (2)$$

where T_{obs} is the average of experimental measurements and T_{ideal} the projected value from an ideal-solution vapor-pressure curve. It is important to note that the actual percent deviation for all three observed mixtures is quite small at all compositions examined. This suggests that even though the mixtures behave differently relative to one another, the absolute value of vapor pressure of each mixture is quite close to that of an ideal solution of the same mole fraction.

Table 4
TGA-derived temperature dependence of vapor pressure for mixtures of of tributyrin (C4 : 0) and tricaproin (C6 : 0)

C6 mole fraction	Sample size/ mg	Pressure/ mmHg	Observed boiling point/ °C	Ideal boiling point/ °C	Deviation [a]/ %
0.2068	8.5	34	205.2	204	0.6
0.2068	8.6	33	202.6	203.1	0.2
0.2068	7.0	104	245.5	240.5	2
0.2068	7.1	102	238.1	239.9	0.7
0.2068	6.8	406	289.2	293.4	1.5
0.2068	8.4	404	287.8	293.2	1.8
0.2068	5.5	761	325.6	321.7	1.2
0.2068	5.8	761	323.6	321.7	0.6
0.2068	4.9	761	326.4	321.7	1.4
0.7012	7.5	28	225.8	220.7	2.3
0.7012	7.1	26	226.9	218.5	3.8
0.7012	7.5	101	240.1	261.9	8.3
0.7012	8.3	107	262.6	263.9	0.5
0.7012	6.4	106	249.6	263.6	5.3
0.7012	8.9	395	319.6	313.9	1.8
0.7012	8.0	398	314.1	314.2	0.0
0.7012	5.1	763	346.4	342.8	1.0
0.7012	9.1	765	340.7	342.9	0.7

[a] Refer to Table 1, footnote.

3.3. Vapor pressure vs. temperature

TGA-derived vapor-pressure data for mixtures of tributyrin/tricaproin and tributyrin/tricaprylin were determined for two different mole fractions from 760 down to 20 mmHg. The standard deviation for replicate runs averaged 1.83%. The results of this analysis are compiled in Tables 4 and 5. In Figs. 7 and 8, these data are used to construct Clausius–Clapeyron plots. For each mixture shown in these figures, it is apparent that the data closely follow the Clausius–Clapeyron model as shown by the fit to a linear regression. Average deviations from the regression line are 2.1%.

From regressions of the Clausius–Clapeyron plots, it was possible to calculate the constants A and B necessary to determine the actual Clausius–Clapeyron equation as follows:

$$\log P = -A/T + B \quad \text{(where } P \text{ is in mmHg and } T \text{ in } K\text{)} \qquad (3)$$

The calculated values of A and B for each mixture and an R^2 value for the regression are given in

Table 5
TGA-derived temperature dependence of vapor pressure for mixtures of tributyrin (C4 : 0) and tricaprylin (C8 : 0)

C8 mole fraction	Sample size/ mg	Pressure/ mmHg	Observed boiling point/ °C	Ideal boiling point/ °C	Deviation [a]/ %
0.1764	6.8	32	204.6	206.0	0.7
0.1764	7.3	33	205.7	206.9	0.6
0.1764	6.5	102	241.5	241.1	0.2
0.1764	5.9	101	245.1	240.8	1.8
0.1764	5.9	400	288.0	289.6	0.6
0.1764	7.9	403	284.6	289.9	1.8
0.1764	7.9	401	289.8	289.7	0.0
0.1764	6	763	319.6	315.9	1.2
0.1764	6.3	765	316.7	316.0	0.2
0.6584	7.3	29	269.3	275.8	2.3
0.6584	7.6	33	265.2	279.4	5.1
0.6584	6.5	72	310.0	302.4	2.5
0.6584	6.4	67	312.0	300.2	3.9
0.6584	8.6	104	327.1	313.9	4.2
0.6584	7.9	107	328.5	314.8	4.3
0.6584	6	107	328.6	314.8	4.4
0.6584	6.8	400	368.7	360.3	2.3
0.6584	4.8	401	366.5	360.4	1.7
0.6584	6.3	563	373.3	373.3	0.0
0.6584	6.8	569	368.3	373.7	1.4
0.6584	5.2	762	376.4	385.2	4.6
0.6584	6.3	763	363.9	385.3	5.5
0.6584	6.5	763	371.2	385.3	3.7
0.6584	5.7	762	369.8	385.2	4.0

[a] Refer to Table 1, footnote.

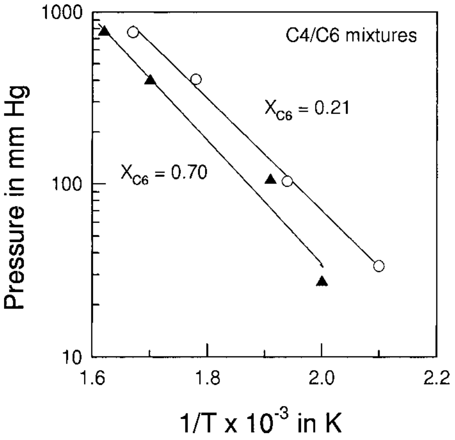

Fig. 7. TGA-derived temperature dependence of vapor pressure for mixtures of tributyrin (C4 : 0) and tricaproin (C6 : 0).

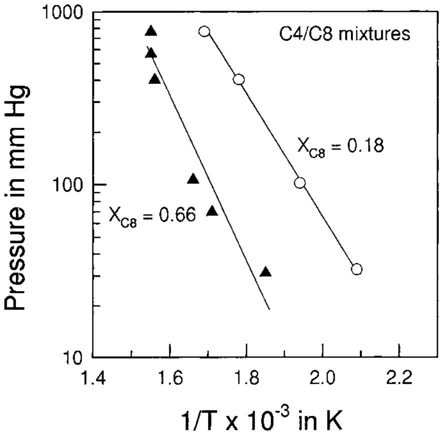

Fig. 8. TGA-derived temperature dependence of vapor pressure for mixtures of tributyrin (C4 : 0) and tricaprylin (C8 : 0).

Table 6. Note that most of the R^2 values are well above 0.90.

3.4. Calculation of enthalpies of vaporization

The vaporization enthalpies (ΔH_v) of the two mixtures (tributyrin/tricaproin and tributyrin/tricaprylin) were determined and are shown in Table 6. ΔH_v was calculated by determining the boiling point for the mixtures at exactly 760 and 30 mmHg from the plot [8]. These values were used with the constant A to determine ΔH_v using the equation:

$$\Delta H_v = 2.3(A)(R), \text{ (where } R = 8.13\,\text{J/g mol K)} \tag{4}$$

As is generally observed for homologous series of compounds, the vaporization enthalpy of triglyceride mixtures increased with the average molecular weight of the mixture.

Despite the fact that these are mixtures of compounds, the TGA method has provided an "effective" boiling-point value. Based on the effective boiling point, an effective solution enthalpy of vaporization is calculated from the Clausius–Clapeyron model. The fact that the boiling points of these solutions closely follow the Clausius–Clapeyron equation gives strong support to this approach for obtaining a ΔH_v for near-ideal solutions.

3.5. Vapor pressures of biodiesel fuels

TGA-derived vapor pressures were also determined for two biodiesels, complex ester mixtures, which have been researched for use as substitute diesel fuels [10]. Fig. 9 is a Clausius–Clapeyron plot for vapor pressure of tallow ethyl ester (TEE). Fig. 10 illustrates the same relationship for rapeseed methyl ester (RME). From these plots it may be seen that these complex mixtures exhibit uniform effective boiling-point behavior similar to the TGA results for binary triglyceride mixtures. The measured vapor pressure of these ester mixtures may be an average value influenced by all of the component esters. The TGA results certainly strongly conflict with the expectation that these mixtures would fractionate into components during vapor-pressure analysis. The uniform behavior

Table 6
TGA-derived temperature dependence of vapor pressure for triglycerides and binary mixtures

Sample	Boiling point [b]/ K	Boiling point [c]/ K	A [d]	B [d]	R^2	ΔH_v [e]/ ($\mathrm{J\,g^{-1}\,mol^{-1}}$)
C4 : 0 [a]	590.94	471.45	3272.95	8.4194	0.9939	62 555.90
C6 : 0	646.43	519.22	3794.98	8.7808	0.9908	72 533.45
C8 : 0	657.76	562.19	5431.18	11.1379	0.9368	103 806.14
C10 : 0 [a]	667.10	594.61	7680.85	14.3939	0.9908	14 795.21
25% C6/C4	594.64	473.21	3252.77	8.3509	0.9938	62 170.19
75% C6/C4	615.64	495.76	3573.65	8.6856	0.9728	68 303.17
25% C8/C4	588.74	477.20	3535.50	8.8860	0.9968	67 574.00
75% C8/C4	656.90	550.00	4743.84	10.1024	0.9135	90 669.01

[a] Data from Goodrum and Siesel (Ref. [3]).
[b] @760 mmHg.
[c] @30 mmHg.
[d] A and B are from linear regression of equation, $\log P = -(A/T) + B$, where T=K.
[e] $\Delta H_v = 2.3(A)(R)$, where $R = 8.31\ \mathrm{J\,g^{-1}\,mol^{-1}}$.

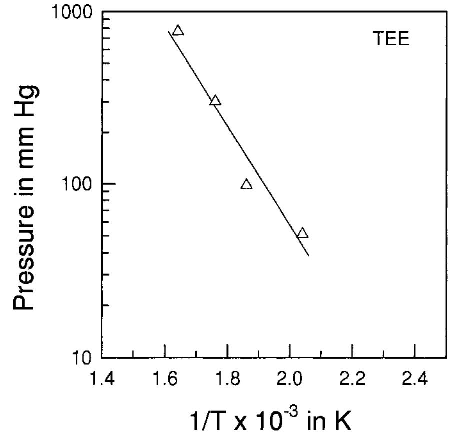

Fig. 9. TGA-derived temperature dependence of vapor pressure for tallow ethyl ester.

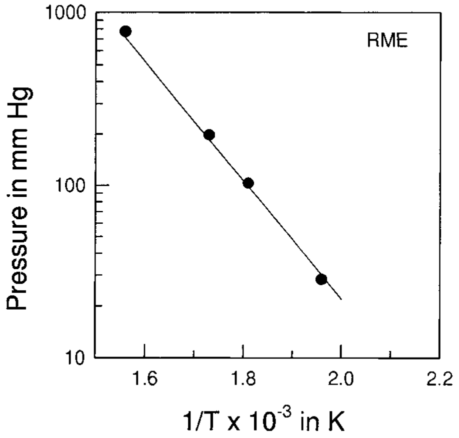

Fig. 10. TGA-derived temperature dependence of vapor pressure for rapeseed methyl ester.

exhibited here may perhaps be explained by the rapidity of the TGA technique or the small sample size used for analysis.

In order to examine the behavior of these biodiesel fuels, one could establish an ideal solution reference curve. In order to accomplish this, the composition of each esterified oil would have to be determined using a technique such as high-pressure liquid chromatography. Once the composition is determined, an ideal curve could be established by weighting the vapor pressure of each component with the percent composition of each component in the ester blends. The deviation from the ideal in these solutions could then be compared to the deviation observed in the binary solutions. From these two data sets it may be possible to establish a pattern in vapor pressure behavior that would depend on the number and identity of components in seed-oil-derived mixtures. This type of model could then be applied to the characterization of potential substitute diesel fuels. For example, near-ideal solution behavior could be used to predict the boiling point of potential substitute-diesel fuels such as seed-oil triglycerides. The authors suggest that it is reasonable to infer this result based on a good agreement with Clausius–Clapeyron behavior, which assumes constant ΔH_v and vapor which behaves as an ideal gas.

4. Conclusions.

1. Thermogravimetric analysis using laser-drilled sample capsules provides rapid, accurate, and precise vapor-pressure and boiling-point data for binary mixtures of short chain triglycerides.
2. The experimental boiling temperatures of these mixtures at 1 atm as a function of composition were determined using TGA. The results showed good agreement with those predicted for ideal mixtures of the same composition. This relationship became more obvious as the chemical similarity of the components in the mixture increased.
3. The TGA measured temperature dependence of vapor pressure for the binary triglyceride mixtures closely followed the linear Clausius–Clapeyron model.
4. TGA analysis of the vapor pressures of biodiesel, alternative diesel fuels composed of complex mixtures of fatty-acid esters, produced consistent, predictable results, generally very similar to results from binary mixtures.

Acknowledgements

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References

[1] C.K.M. Msipa, C.E. Goering, T.D. Karcher, Trans. ASAE 26(6) (1983) 1669.

[2] J.W. Goodrum, M.A. Eiteman, Bioresource Technology 56 (1996) 55.

[3] J.W. Goodrum, E.A. Siesel, J. Therm. Anal. 46 (1996) 1251.

[4] R.J. Seyler, Thermochim. Acta 17 (1976) 129.

[5] B. Cassel, M.P. Divito, American Laboratory, January 1994, p. 14.

[6] K. Jones, R.J. Seyler, NATAS Notes 26(2) (1994) 61.

[7] R.C. Perry, C.H. Chilton (Eds.), Chemical Engineer's Handbook, 6th edn., McGraw-Hill, New York, 1984, pp. 3–59.

[8] E.S. Perry, W.H. Weber, B.F. Daubert, J. Amer. Chem. Soc. 71 (1949) 3720.

[9] W.J. Moore, Physical Chemistry, 3rd edn., Prentice Hall, Englewood Cliffs, N.J., 1965, pp. 128–129.

[10] C.L. Peterson, D.L. Reece, B.L. Hammond, J. Thompson, S.M. Beck, paper presented at ASAE meeting, Dec 13–16, 1994, St. Joseph, MI.